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FOR

CARBON MONOXIDE SENSOR AND METHOD OF USE

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TECHNICAL FIELD OF THE INVENTION

This invention relates to a sensor that is capable of detecting low concentrations of carbon monoxide (CO) in a relatively hydrogen-rich and relatively oxygen-free gas mixture. The sensor can be used within a wide variety of systems

15   presenting this type of environment, such as fuel processors for PEM fuel cell power generation systems that are being developed for automotive, residential, and other applications.

BACKGROUND OF THE INVENTION

20   Fuel cells are being developed as power sources for many applications. Fuel cells generate power, without combustion, by extracting the chemical energy of hydrogen from hydrogen containing fuels. Advantages of fuel cells include high efficiency and very low release of polluting gases (e.g., NO_x) into the atmosphere. Of the various types of fuel cells, the proton exchange membrane (PEM) fuel cell is

25   receiving considerable attention for transportation applications due to its low weight, low temperature operation, and its considerable potential for mobile and residential applications. The heart of the PEM fuel cell is a membrane electrode assembly

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(MEA), which is a sheet of a proton-conducting polymeric material (e.g., Nafion) with thin coatings of platinum containing electrocatalysts (anodes and cathodes) on opposite faces. Several MEAs are stacked with interposed electrically conductive elements (current collectors) that contain appropriate channels for distributing the gaseous reactants over the surfaces of the anode and cathodes. PEM fuel cells operate most efficiently when hydrogen is the anode reactant (fuel) and oxygen as the cathode reactant (oxidant). However, for more practical applications, air is used as the oxidant and a hydrogen rich gas (derived from hydrocarbons) is used as the fuel. For transportation applications, the use of liquid hydrocarbon fuels for fuel cells, such as gasoline, is most attractive due to transportability, high energy density, and existing infrastructure.

One of the problems of using hydrocarbons to produce the hydrogen required for operating the PEM fuel cell is that carbon monoxide is a poison to the platinum electrocatalysts in the anode of the MEA. Performance of the PEM fuel cell can be degraded when CO is present at levels as low as 20 parts per million, and considerable performance degradation is observed when the CO content is higher than 100 parts per million. Thus, the hydrocarbon fuels must be converted into a hydrogen rich gas containing little or no carbon monoxide (since trace amounts of CO will degrade PEM fuel cell performance). Fuel processors, utilizing multiple catalytic reactor stages, are being developed to meet this requirement. For the automotive application, especially, It will be imperative to have a sensor that monitors the amount of carbon monoxide at various stages of the fuel processing system, and to monitor CO content of the hydrogen-rich gas exiting the fuel processor.

The importance of carbon monoxide sensors for automotive PEM fuel cell systems is illustrated by a schematic of an automotive fuel processor, shown In

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Figure 1. Fuel processing **10** typically involves three or four catalytic stages. The first reforming step **14** involves the reaction of gasified hydrocarbons **12** with air **11** (partial oxidation or POX), or with air **11** and steam **13** (autothermal reforming or ATR), to convert gasoline, methanol or other hydrocarbons into a gas mixture rich in hydrogen and carbon monoxide. This reformed gas mixture then is subjected to the water-gas-shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) to reduce carbon monoxide levels and increase hydrogen content. The water-gas-shift (WGS) reaction is usually performed in two separate reactions, the first **15** at relatively high temperature (to convert most of the carbon monoxide), and the second **16** at a lower temperature (where equilibrium CO contents are lower). After exiting the WGS reactors **15** and **16**, the hydrogen-rich reformate gas enters the preferential oxidation (PROX) reactor **17** where the gas is mixed with air **11** to oxidize remaining carbon monoxide to carbon dioxide. A key technical challenge facing developers of fuel processors for automotive applications is the requirement to maintain low carbon monoxide contents during operational transients, such as those that would occur during acceleration and deceleration. Transients can cause spikes in the carbon monoxide content of the reformed gas. The primary use for the CO sensors under development in this program is to measure the CO content of the reformate gas **18** exiting the PROX reactor **17**. There are two potential benefits of this type of CO sensor:

(1)   The sensor can provide feedback to the PROX reactor. This will allow the optimum amount of air to be fed into the PROX reactor (and minimize any wasted hydrogen); and

(2)   The sensor will protect the PEM fuel cell stack. When a high CO content is detected the reformate gas would be diverted from the stack (with power being provided by a battery) until the CO level returns to tolerable levels.

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Existing carbon monoxide sensors cannot meet the requirements of the fuel cell application. Commercial CO sensors, typically based on semiconducting oxides (e.g., tin oxide), operate on the basis of a resistance change due to oxidation of CO to CO_2 (carbon dioxide). This type of sensor cannot work for the fuel cell application

5   because of the absence of oxygen in the reformate gas. Further, even if oxygen were available, it would be difficult for the tin oxide sensor to detect low levels of carbon monoxide in the presence of a high concentration of hydrogen (because oxidation of hydrogen also will occur). With current technology, optical sensors are the only current option for rapid and accurate detection of CO in a hydrogen-rich

10   atmosphere. However, optical sensors are bulky and extremely expensive, and it is doubtful that the size and cost of these systems can be reduced sufficiently for the fuel cell application.

It is therefore a goal of the present invention to provide a sensor that can detect carbon monoxide in a hydrogen-rich oxygen-deficient environment. That is to

15   say, it is an object of the present invention to provide a sensor that can detect carbon monoxide in a reducing environment. It is a further goal of the present invention to provide a sensor that can detect carbon monoxide in a hydrogen-rich gas stream so as not to poison the catalyst of a PEM fuel cell.

20   **SUMMARY OF THE INVENTION**

The present invention presents a novel approach for detection of low levels of carbon monoxide in hydrogen-rich gas mixtures. The approach is based on the change in electrical resistance that occurs when carbon monoxide is selectively absorbed by a thick film of copper chloride (or other metal halides). The resistance

25   change was shown to occur rapidly with both increasing and decreasing CO contents, to vary with the amount of CO from the gas stream, and was insensitive to

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the presence of hydrogen. The present invention includes a sensor and methods of using the sensor to measure the concentration of CO in a gas stream.

A sensor for determining the concentration of carbon monoxide in a gas stream as a function of measured resistance of the present invention comprises a

5   non-conductive substrate, having a first and a second side, onto which a first and a second electrode are deposited on the first side such that the first electrode is not in contact with the second electrode. A sensing material is in electrical contact with the first electrode and the second electrode. The sensing material is a metal halide capable of absorbing carbon monoxide from the gas stream and has an electrical

10   resistance that varies in proportion to the absorbed carbon monoxide on the sensing material.

It is preferred that sensors of the present invention employ alumina substrates. However, it should be noted that any non-conductive suitable material may be used for the substrate. Additionally, it is preferred that the first and the

15   second electrode are interdigital electrodes disposed so as not to touch one another. It is preferred that the first and second electrodes are made of gold or copper. Further, it is preferred that the sensing material is comprised of a majority of cuprous chloride (CuCl) and a minority of a copper halide wherein the copper of the copper halide has a valence of at least +2. It is most preferred that the sensing material is

20   cuprous chloride. It is preferred that sensors of the present invention further comprise a heater deposited on the second side of the substrate and adapted to maintain the sensor at a substantially constant temperature. It is most preferred that the heater is a platinum heater. Additional methods of temperature control may be employed to assist the heater in maintaining a constant sensor temperature such as

25   computer control or other known methods. With respect to sensors of the present invention based upon copper, these sensors operate best when they are used in a

substantially water-free environment. It is most preferred that copper-based sensors of the present invention are used in a water-free environment. In cases where the function of copper-based sensors is adversely affected by exposure to water, it has been found that function may be restored by removal of the water.

5   A method for using a sensor of the present invention to determine the concentration of carbon monoxide in a gas stream begins by passing a gas stream to a sensor (as described above) with a potential impressed across the first electrode and the second electrode. A measurement may then be taken of the resistance of the sensing material. The resistance of the sensing material is dependent to the

10   concentration of carbon monoxide in the gas stream and may be outputted to a device. It should be noted that a measurement may be taken of any electrical property dependent on the concentration of carbon monoxide in the gas stream. Alternatives to the measuring of resistance include, but are not limited to: conductance and impedance.

15   In a preferred method of the present invention the device is a display device adapted to provide a read-out of the carbon monoxide concentration based on the measured resistance. It is additionally preferred that the device be a controller adapted to adjust the gas stream in response to the outputted resistance measurement.

20   A second method for sensing the concentration of carbon monoxide during the conversion of fossil fuel to into a gas stream using a sensor of the present invention comprises the reacting of a flow of gases to produce a gaseous mixture of hydrogen, carbon dioxide, carbon monoxide, nitrogen, and water. The reacted flow of gases is then sent to at least a first reactor adapted to reduce carbon monoxide

25   content and increase hydrogen content, thereby forming a reformate gas. The reformate gas is then sent to at least a second reactor adapted to combine a flow of

air with the reformate gas so as to oxidize carbon monoxide to carbon dioxide and so as to not oxidize the hydrogen to water. The oxidized flow of air and reformate gas is then passed to a sensor of the present invention (as described above) where the resistance of the sensing material is measured. The measured resistance is used to

5   provide feedback to the at least second reactor. The resistance of the sensing material provides a measure of the concentration of carbon monoxide in the gas stream and the at least second reactor is adapted to adjust the flow of air in response thereto.

It is preferred that the method additionally comprises the step of directing the

10   oxidized flow of air and reformate gas to a next device. It is more preferred that the method further comprises the step of diverting the oxidized flow of air and reformate gas from the next device when the concentration of carbon monoxide detected by the sensor exceeds a threshold. Suitable next devices may include a PEM fuel cell or storage tank, although other suitable next device may be obvious to one skilled in

15   the art.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic of an automotive fuel processor that a sensor of the present invention may be used on.

20   Figure 2 shows the bottom face of a sensor in accordance with one embodiment of the present invention.

Figure 3 shows the top face of a sensor in accordance with one embodiment of the present invention.

Figure 4a is a SEM micrograph of copper chloride film prepared in

25   accordance with one method (Method 1) of the present invention.

Figure 4b is a SEM micrograph of copper chloride film prepared in accordance with one method (Method 1) of the present invention.

Figure 4c is a SEM micrograph of copper chloride film prepared in accordance with one method (Method 2) of the present invention.

5   Figure 4d is a SEM micrograph of copper chloride film prepared in accordance with one method (Method 2) of the present invention.

Figure 5 is a CO sensitivity graph of CuCl film sample of Method 1B at 50° C in N_2.

Figure 6 is a CO sensitivity graph of CuCl film sample of Method 1B at 50° C

10   in the presence of H_2.

Figure 7 is a CO sensitivity graph of CuCl film samples of Method 2 at 50° C in the presence of H_2.

Figure 8 shows the detection of different CO levels in a H_2/N_2 atmosphere at 50° C (samples produced by Method 2).

15   Figure 9 illustrates the response time of a metal halide sensor manufactured by a thick film deposition technique.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

A novel approach for detection of low levels of carbon monoxide in hydrogen-

20   rich gas and oxygen-deficient mixtures is provided below. The approach is based on the change in electrical resistance that occurs when carbon monoxide is selectively absorbed by a thick film of copper chloride (or other metal halides). This resistance change was shown to occur rapidly with both increasing and decreasing CO contents, to vary with the amount of CO from the gas stream, and was insensitive to

25   the presence of hydrogen. Hydrogen-rich gas streams contain at least 10% hydrogen (H_2). Oxygen-deficient gas streams contain less than 0.5% oxygen (O_2).

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The gas stream in which the sensor is used has a reducing nature. That is to say, the gas stream contains substantially no oxidizing gases such as oxygen. The gas stream has a reducing nature due to the presence of hydrogen or other reducing gases. For the purposes of this application, hydrogen is representative of a reducing gas and oxygen is representative of an oxidizing gas.

The preferred operating temperature of sensors of the present invention is a temperature at or above the gas stream temperature.

Turning to Figures 2 and 3, a preferred sensor of the present invention is presented. Figures 2 and 3 respectively illustrate the bottom and top faces of a preferred sensor in accordance with one embodiment of the present invention. Figure 2 details the bottom face **22** of preferred sensor **20**. The sensor **20** is preferably constructed from an alumina substrate **26** upon which a thick-film platinum heater **24** is preferably deposited. In addition to alumina, the sensor substrate may be any suitable ceramic or non-conductive material. Figure 3 shows the top face **32** of sensor **20**. The top face **32** of sensor **20** has a first interdigital electrode **34** and a second interdigital electrode **35**. The interdigital electrodes, **34** and **35**, are preferably constructed of gold. However, the interdigital electrodes, **34** and **35**, may be made of copper or any other suitable conducting material. The sensing material **36** is preferably deposited onto the top face **32** of sensor **20** so as to cover an area containing the interdigital electrodes **34**. The sensing material **35** is preferably constructed of copper chloride (CuCl) formed by one of the fabrication methods outlined below. However, the sensing material **35** may be formed from any metal halide whose electrical resistance is dependent upon CO absorption.

The thick-film platinum heater **24** is adapted to supply heat to the sensor **20** to maintain constant temperature. A constant sensor temperature ensures that the

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output of the sensor is consistent and accurate, as resistance is a function of temperature.

The sensor determines the presence of CO in the gas stream by measuring the resistance between the first interdigital electrode **34** and the second interdigital

5   electrode **35** across the sensing material **36**.

FABRICATION PROCESSES

Different fabrication methods were evaluated for preparing copper chloride (CuCl) films. The films were deposited onto alumina substrates with gold IDE

10   electrodes, and the CO sensing performance was evaluated. Varying degrees of copper chloride sensitivities were observed in copper chloride films prepared by the five methods. The best results were obtained with pure copper chloride film prepared by Methods 1 and 2, which are described below:

Method 1: CuCl in Acetonitrile Drop Deposition. With this method, 50 mg of

15   "purified" CuCl was first dissolved in 5 ml of acetonitrile, with nitrogen bubbling through the solution to prevent any aerial oxidation. An IDE substrate was placed on a hot plate and heated to 90°C, a temperature above the boiling point of acetonitrile (82° C). The CuCl solution was added dropwise to the hot IDE, allowing the acetonitrile to evaporate, leaving a CuCl film. The drops were added until reasonable

20   film thickness was obtained. Two types of CuCl film samples were prepared: films deposited with nitrogen bubbling through the acetonitrile solution and drying under nitrogen (anaerobic) and films deposited with bubbling nitrogen and drying in air (aerobic). The CuCl films prepared under the anaerobic condition were white (presumably pure copper chloride), whereas films produced under the aerobic

25   condition were grayish-white (presumably due to partial oxidation).

Method 2: CuCl in Acetonitrile Solvent Evaporation Deposition. This method involved the initial preparation of a solution of 75 mg of purified CuCl in 5 ml of acetonitrile, as, described above. An IDE-alumina substrate was placed in a 10-ml beaker and submerged in the CuCl/acetonitrile solution. The beaker was placed in a vacuum oven at room temperature to evaporate the acetonitrile. During the removal of the acetonitrile, the CuCl physically precipitates onto the IDE substrate. The sample was vacuum dried until all solvent was removed. Film samples produced by this method were grayish white, possibly due to film oxidation when the beaker was transferred into the vacuum oven.

X-ray diffraction data obtained on copper chloride films prepared by the above methods indicated single-phase copper chloride (CuCl) with the expected nantokite structure. The microstructures of film samples prepared from CuCl/acetonitrile solutions were evaluated by scanning electron microscopy (see Figures 4a through 4d). Very striking differences in the morphology of the two samples were observed. The sample prepared by Method 1 (dropwise addition of the acetonitrile solution onto a heated substrate) exhibited a highly porous structure of spherical CuCl particles (see Figures 4a and 4b), whereas the film sample produced by Method 2 (direct precipitation of CuCl during evaporation of acetonitrile) exhibited a lamellar structure, with laminae comprised of very small spherical CuCl crystals (see Figures 4c and 4d). The CO sensing performance of copper chloride film samples were evaluated. Results of sensor evaluations are described below.

Sensor 1A (Casting from "Anaerobic" CuCl/Acetonitrile Solutions). The CO sensing performance of samples prepared by Method 1 (i.e., drop-wise casting of CuCl/acetonitrile solutions onto heated IDE-alumina substrates) was evaluated for nitrogen and nitrogen/hydrogen gas atmospheres. The first sample that was tested was a CuCl film sample prepared under purely "anaerobic" conditions (i.e., with

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nitrogen bubbling through the acetonitrile solution during film casting). Before testing, this sample was reduced in hydrogen for two hours at 150° C. This sample exhibited no response whatsoever to CO at 50° C.

Sensor 1B (Casting from "Aerobic" CuCl/Acetonitrile Solutions). A CuCl film sample prepared by Method 1 was prepared under "aerobic" conditions (the film was deposited from an acetonitrile solution and dried in air). This sample also was reduced in hydrogen as described previously. The film sample exhibited strong responses to CO, both in nitrogen and nitrogen/hydrogen atmospheres (see Figures 5 and 6). Figure 5 shows the CO sensitivity of a CuCl film sample of Method 1B at 50° C in N_2. The resistance of a sensor was tracked through periods of pure N_2 **50** interrupted by periods of 1000-ppm CO gas **52**. Figure 6 shows the CO sensitivity of CuCl film sample of Method 1B at 50° C in the presence of H_2. The resistance of a sensor was tracked through periods of N_2/H_2 **60** interrupted by periods of CO gas **62**. The response of the sensor to 1000-ppm CO was stable for many cycles. The hydrogen gas concentration was varied from 0 to 50% and absolutely no change in the baseline resistance or CO sensitivity was observed.

Sensors Prepared by Method 2 (CuCl/Acetonitrile Solvent Evaporation). The CO sensing performance of a CuCl film sample prepared by Method 2 (direct precipitation of CuCl by evaporation of acetonitrile solutions) was evaluated in a H_2/N_2 atmosphere. Before testing, the sample was reduced in hydrogen for two hours at 150° C. This sample exhibited a very strong and repeatable on/off response to carbon monoxide at 50° C, as shown in Figure 7. Figure 7 shows the CO sensitivity of CuCl film sample of Method 2 at 50° C in the presence of H_2. The resistance of a sensor was tracked through periods of N_2/H_2 (0-ppm CO) **70** interrupted by periods of 1000-ppm CO gas **72**. The resistance decreased in the presence of CO and then increased (returning to baseline) upon nitrogen/hydrogen

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purge. During sensor testing, the hydrogen content was varied between 25 and 75 vol%, and there was no change in the baseline resistance. Further, this sensor was able to detect CO over the range of 500 to 1500 ppm, as shown in Figure 8. Figure 8 illustrates the detection of different levels of CO in a N_2/H_2 atmosphere at 50° C

5 using a sensor of Method 2. The resistance of the sensor during periods of N_2/H_2 **80** is higher than the resistance when 500 ppm of CO gas **82** is introduced. Further, the resistance dropped again when the CO gas was increased to 1000-ppm **84**. The resistance dropped for a third time as the CO gas was increased to 1500-ppm **86**. The response of this sample to CO was reproducible over many cycles, without

10 exhibiting any signs of degradation.

Figure 9 shows the CO sensitivity of a metal halide sensor manufactured by a thick film deposition technique described above. The resistance of the sensor was tracked through periods of H_2/N_2, interrupted by periods of 5000-ppm carbon monoxide gas. The sensor exhibited extremely fast response times, of about one

15 second, in the presence of CO.

While we have shown that active CO sensors can be produced using chemical deposition methods, multiple deposition techniques would also be viable for producing CO sensors of the present invention, i.e. using metal halide based materials. Multiple deposition techniques include: pellet pressing, spin-coating, dip-

20 coating, tape-casting, screen printing, radio-frequency (R.F.) sputtering, direct-current (D.C.) sputtering, reactive magnetron sputtering, and chemical vapor deposition (CVD) methods among others.

The above results indicate that the electrical resistance of certain copper chloride films can be very sensitive to carbon monoxide and insensitive to hydrogen,

25 and that rapid responses are indeed possible. These are critical criteria for any CO sensing approach for automotive fuel cell applications. The results obtained also

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showed the importance of film fabrication methods on the electrical resistance and

CO sensing performance of CuCl films. Baseline electrical resistance values of CuCl

films varied over three orders of magnitude, depending on the film fabrication

method. Further, the presence of (and the longevity of) measurable resistive

5   responses to CO also varied with fabrication method.

While the invention has been described in connection with what is presently

considered to be the most practical and preferred embodiments, it is to be

understood that the invention is not to be limited to the disclosed embodiment, but on

the contrary, is intended to cover various modifications and equivalent arrangements

10   included within the spirit and scope of the appended claims, which are incorporated

herein by reference.